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A Valence Bond Model for Electron-Rich Hypervalent Species: Application to SF_n (*n* = 1, 2, 4), PF₅, and ClF₃

Benoit Braida,^{*,[a, c]} Tristan Ribeyre,^[a] and Philippe C. Hiberty^{*,[b]}

Abstract: Some typical hypervalent molecules, SF₄, PF₅, and ClF₃, as well as precursors SF (⁴Σ[−] state) and SF₂ (³B₁ state), are studied by means of the breathing-orbital valence bond (BOVB) method, chosen for its capability of combining compactness with accuracy of energetics. A unique feature of this study is that for the first time, the method used to gain insight into the bonding modes is the same as that used to calculate the bonding energies, so as to guarantee that the qualitative picture obtained captures the essential physics of the bonding system. The ⁴Σ[−] state of SF is shown to be

bonded by a three-electron σ bond assisted by strong π back-donation of dynamic nature. The linear ³B₁ state of SF₂, as well as the ground states of SF₄, PF₅ and ClF₃, are described in terms of four VB structures that all have significant weights in the range 0.17–0.31, with exceptionally large resonance energies arising from their mixing. It is concluded that the bonding mode of these hypervalent species and isoelectronic ones complies with Coulson's version of the Rundle–Pimentel model, but assisted by charge-shift bonding. The conditions for hypervalence to occur are stated.

Introduction

Sulfur, phosphorous, and chlorine atoms, as well as elements below them in the periodic table and heavier noble gases, have the ability to form more bonds than allowed by the traditional Lewis–Langmuir valence rules; this property is referred to as hypervalence.^[1] By contrast, lighter elements of the family strictly obey the octet rule, showing what has been called the “first-row anomaly”.^[2] The first tentative explanation for the hypervalence of P and S atoms was proposed by Pauling in terms of an expanded octet model, through promotion of electrons into vacant high-lying *d* orbitals, leading to *sp*³*d* hybridization.^[3] However, it has been shown by many researchers^[3–5] that *d* orbitals do not act primarily as valence orbitals, but instead as polarization functions or as acceptor orbitals for back-donation from the ligands, thus disproving the expanded octet model. On the other hand, the most widely accepted model for electron-rich hypervalence is the Rundle–Pimentel model, which does not require *d*-orbital participation.^[6] In the molecular orbital (MO) framework, this model is based on

a general three-center, four-electron (3c–4e) molecular system, made of three atoms or fragments that each contribute a single AO from which a set of three MOs is constructed. In the general case of 3c–4e species, three pure *p_z* orbitals (or *s* orbitals in the H₃[−] case) combine to form the set of MOs φ₁–φ₃ in Scheme 1, which are bonding, nonbonding, and anti-

Scheme 1. The MO-based Rundle–Pimentel model for 3c–4e hypervalent complexes.

bonding, respectively. The first two are occupied, so the system is bonding overall with a net bond order of 0.5 for each linkage. The Rundle–Pimentel model served to rationalize and predict many structures, but was also considered as oversimplified by Hoffmann and colleagues, because it only considers the axial *p* atomic orbitals (AOs) and ignores their mixing with the underlying *s* AOs.^[7] A consequence of this oversimplification is that the model would tend to predict all 3c–4e systems to be stable, hence failing to explain not only the above-mentioned “first-row anomaly”, but also the instability of, for example, ArF₂.

Even more problematic for the Rundle–Pimentel model is its failure to account for the instability of the simplest 3c–4e system, H₃[−], which is a transition state in the H[−] + H₂ → H₂ + H[−] exchange reaction, lying 11 kcal mol^{−1} above the reactants,^[8] although the isoelectronic F₃[−] is stable. To quote Kutzelnigg,^[9] “Whereas simple MO theory has no difficulty in describ-

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ing three-center, two-electron bonds such as that in H_3^+ , problems do arise in the description of three-center, four-electron bonds since for H_3^- it incorrectly predicts a strong bond with respect to H_2 and H^- . The failure of simple MO theory for H_3^- is not easy to understand".

The Rundle–Pimentel model was also expressed in terms of "increased valence structures" by Harcourt,^[10] and was turned into a traditional valence bond (VB) form by Coulson.^[11] Thus, this author showed that a trivial expansion of the $\varphi_1^2\varphi_2^2$ configuration into VB structures leads to a VB form of the Rundle–Pimentel model [Eq. (1)] for an X–A–X (3c–4e) linear arrangement, in which the "—" sign stands for a covalent bond.

Interestingly, Coulson's model is not bound to neglect s,p mixing in the AOs, as any s,p hybridization is allowed in the orbitals of the VB structures in Equation (1), so in this sense it can be considered more general than the original MO-based Rundle–Pimentel model (Scheme 1). Now, this model explains the stability of the hypervalent species in terms of the resonance energy that arises from the mixing of the various VB structures, but gives no indication of the magnitude of this resonance energy or what factors are expected to favor it.

Recently, an important step forward was made by Woon and Dunning, who showed that the building block of the SF_n species is the SF diatomic molecule in an excited state, actually the $^4\Sigma^-$ state, denoted SF* herein.^[12] This state, although significantly bonded, leaves two free valences (singly occupied π AOs), thus opening the possibility of higher coordination. Then, adding a fluorine atom to sulfur in a linear fashion leads to another excited state, the 3B_1 state of SF_2 (denoted FSF* or SF_2^*), which is a hypervalent species in that it leaves two free valences that can readily accept further ligands.

From a qualitative analysis based on generalized valence bond (GVB) calculations, the authors coined the term "recoupled-pair bonding" to designate the bonding mechanism accounting for the stability of SF* and SF_2^* , and, by extension, of the linear FSF fragments in SF_n ($n=2-6$). The same idea, which was deemed by the authors more explanatory than the Rundle–Pimentel model, was then extended to PF_n , ClF_n , and other isoelectronic compounds.^[13–15] To summarize, we are left with three models for hypervalence: 1) the original MO-based Rundle–Pimentel model, 2) its VB variant, which we will call the Coulson–Rundle–Pimentel (CRP) model in this work, and 3) the recent theory of Recoupled-Pair Bonding (RPB). This abundance of apparently competing models calls for clarification and quantitative tests.

One difficulty in trying to interpret computational results in terms of simple bonding mechanisms is that the calculations used to calculate the bonding energies are made at a much higher level than those on which the qualitative interpretation is based. Thus, the basis for the MO-based Rundle–Pimentel model (Scheme 1) is a single Hartree–Fock configuration that completely lacks electronic correlation. On the other hand, the recoupled-pair bonding model is based on GVB, a VB level that

includes static correlation but not dynamic correlation, which is important in hypervalent bonding.^[16,17] Moreover, the GVB calculations are restricted to a single VB structure, whereas four may be necessary to describe the CRP model in Equation (1). Thus, it appears that the best way to establish a qualitative bonding mechanism is to use a unique computational method that combines compactness and interpretability of the wavefunction, to gain insight with reasonable accuracy of the calculated interaction energies so as to validate the qualitative picture. The breathing-orbital valence bond (BOVB) approach is one such method,^[18,19] which is able to describe an interacting system in terms of a few VB structures, and includes not only static correlation, but also the necessary dynamic correlation. Alternatively, a combination of VB with Quantum Monte Carlo methods can also be used for that purpose, and served to prove that the bonding model at work in XeF_2 is well described by the CRP model [with approximately equal weights of the four VB structures of Eq. (1)], assisted with charge-shift bonding, leading to a very large resonance energy that is the main factor responsible for the stability of this compound. Can this bonding mechanism be generalized to other hypervalent electron-rich systems? If the answer is yes, how does recoupled-pair bonding fit in this model? What are the key properties that makes some 3c–4e systems stable and others unstable (e.g., H_3^- , "first-row anomaly", ArF_2 , and so on)? Finally, why are some hypervalent species so strongly bonded, although they violate the octet rule? It was with the aim of answering these questions that we decided to investigate the nature of bonding in some typical electron-rich hypervalent systems, that is SF_4 and its precursors SF* and SF_2^* , as well as isoelectronic PF_5 and ClF_3 , by means of the BOVB method. It is important to note that the qualitative analysis of the wavefunctions will be performed at the same computational level as that used to calculate the bonding energies. Thus, the correctness of the proposed bonding mechanism will be guaranteed by the accuracy of our calculated energetics at each step of bond formation, for example, $S+F \rightarrow SF^*$, $SF^*+F \rightarrow SF_2^*$, $SF_2+2F \rightarrow SF_4$, and so on.

Results and Discussion

The building blocks of hypervalent SF_n : SF ($^4\Sigma^-$) and linear SF_2 (3B_1)

The $^4\Sigma^-$ excited state of SF (SF* for short) is the building block of all the SF_n series, so it is of paramount importance to understand fully its electronic structure and the way the two atoms are bonded. Unlike the ground state of SF, the two atoms do not form a two-electron σ bond, as the sulfur atom presents a lone pair in front of the singly occupied orbital of fluorine, and the two π AOs are both singly occupied and triplet-coupled, as schematized in structure 1 (Scheme 2). In such a configuration, the σ bond, if any, can only be of the three-electron (3e) bonding type, that is, displaying an electron shift between the two σ AOs, as represented in the resonating scheme $1 \leftrightarrow 2$. Such a bond is stabilizing if, and only if, a large resonance energy arises from the mixing of the VB structures 1 and 2,

Scheme 2. The eight possible VB structures of $^4\Sigma^-$ SF* with their weights, as calculated with the BOVB method. The π AOs of the horizontal plane are represented by open circles. The σ lone pairs are not shown.

which may happen if **1** and **2** are quasidegenerate, and implies comparable weights in the VB wavefunction. Scheme 2 shows that this is indeed the case, with weights of 0.34 and 0.42 for **1** and **2**, respectively. Now the two π systems of SF* also have three electrons each for two AOs, and therefore may also form 3e bonds of the π type by left–right shifting an electron as in $2 \leftrightarrow 3$ or $2 \leftrightarrow 4$, in which the σ system is unchanged but one electron has shifted from right to left in one of the π systems. Taking all the possible left–right electron shifts leads to the eight VB structures displayed in Scheme 2. How important is this electron shift in the π system? This can be appreciated by comparing the weights of the major VB structure, **2**, with those of **3** or **4** in which the σ system is unchanged but one electron has shifted from right to left in one of the π systems. The relative weights, 0.42 and 0.10, respectively, are not quasi-equal, but the lowest one is far from negligible, indicating that the three-electron bonding interaction is significant in both π systems. It is important to note that the two π systems are not simply polarized, but undergo some dynamic electron fluctuation that follows the fluctuations of the σ electrons. Thus, simple inspection of the weights of the VB structures in Scheme 2 points to a description of SF* in terms of a triple 3e bond involving a strong 3e σ bond and two weaker π bonds. Alternatively, the bonding mechanism may also be considered as a 3e σ bond assisted by a significant π back-donation of dynamic nature. At this point, this picture still has to be confirmed by calculations of bonding energies.

Table 1 reports some dissociation energies for SF*, as calculated at two different VB levels and in various basis sets. The difference between the VBSCF^[20] and BOVB levels is that the latter includes dynamic electron correlation, whereas the former does not. It can be seen that VBSCF yields much too small dissociation energies, actually close to zero, whereas BOVB provides values some 20 kcal mol⁻¹ larger, showing the paramount importance of dynamic correlation in the bonding mechanism. On the other hand, the BOVB value in the best basis set (of triple-zeta quality), 26.3 kcal mol⁻¹, is fairly close to the landmark CCSD(T) value in the same basis set, 31.0 kcal mol⁻¹, showing that the six-structure VB wave function displayed in Scheme 2 essentially captures the bonding mechanism of SF*.

Table 1 also reports energies calculated with a restricted number of VB structures. The most stable one is structure **2**, of

Table 1. Dissociation energies^[a] for the reaction SF* $\rightarrow$ S + F from VB calculations involving the full set of structures (**1–6**) or a restricted set thereof. Energies in kcal mol⁻¹ relative to the separate atoms.

	VBSCF	BOVB
1–6 (6-31G*)	–2.0	+17.9
1–6 (cc-pVTZ)	+1.8	+24.5
1–6 (VTZ)		+26.3
1–2 (VTZ)		+6.5
2 (VTZ)		–49.2

[a] CCSD(T) reference in VTZ basis set: 31.0 kcal mol⁻¹.

the type S⁺F⁻, having the largest weight (Scheme 2). Mixing it with the neutral structure **1** leads to **1** + **2** and brings a stabilization of 55.7 kcal mol⁻¹, a large quantity typical of 3e σ bonds. Allowing further fluctuation of the π electrons by adding structures **3–6**, brings another 19.8 kcal mol⁻¹, giving a total resonance energy of 75.5 kcal mol⁻¹ relative to structure **2**. Bonds in which most or all of the bonding energy is due to the resonance energies are called “charge-shift bonds”,^[21] of which 3e bonds are a particular case. The reason for such a large resonance energy lies in the quasidegeneracy of structures **1** and **2**, as indicated by their weights in the VB wavefunction, which maximizes the resonance energy arising from their mixing. This quasidegeneracy is made possible by the large difference in electronegativities of the S and F atoms, which makes the electron transfer from S to F very easy. By contrast, the electronegativities of oxygen and fluorine do not differ much, thus preventing the O $\rightarrow$ F electron transfer and immediately explaining why the $^4\Sigma^-$ excited state of OF (isoelectronic to SF*) is very weakly bound.^[15]

All in all, both VB structure weights and resonance energies point to a description of SF* in terms of a triple charge-shift 3e bond, involving a strong 3e σ bond and two weaker π ones, the latter nevertheless being crucial for the stability of this species. Alternatively, one may also consider the bonding mechanism of SF* as a 3e σ bond assisted by significant π back-donation of dynamic nature.

The electronic structure of hypervalent SF₂*, the 3B_1 state of linear SF₂, is easily deduced from the two major VB structures of SF*, as shown in Equation (2).

The addition of an F* radical to (2) in a linear fashion leads to Equations (3) and (4).

Adding to the covalent bond in (4) its polar component leads to the fully ionic structure F: $\text{S}^{2+} : \text{F}^-$, and finally, F: $\text{S}^{+} - ^*\text{F}$ must be added to match the symmetry of the molecule. Thus, we are quite naturally led to the four VB structures **9–12** displayed in Scheme 3, in which the unpaired electron in each

Scheme 3. VB structures of linear 3B_1 SF_2^* and their weights, as calculated with the BOVB method.

π system is represented as being located on the central sulfur atom for simplicity, but must be delocalized to some extent. Structures 9–12 correspond closely to the CRP model of Equation (1). It should be noted that the electronic structure of SF_2^* is intimately linked to that of SF^* . Indeed, the quasi-equivalence of the weights of 1 and 2 in SF^* implies that structures 9, 10, and 12 in SF_2^* should also have comparable weights, hence favoring large stabilizing resonance energies. By contrast, a small weight of 2 relative to 1, as can be anticipated for OF^* , would lead to small weights for 9 and 10 and to instability of the 3c–4e system.

Structures 9–12 form a complete and sufficient set to describe a 3c–4e system, so we used them to calculate the electronic structure of SF_2^* by the BOVB method. For the sake of simplicity, we optimized the geometry of SF_2^* in a constrained linear form (Figure 1), because CCSD(T)/VTZ calculations showed that this geometry lies only $0.4 \text{ kcal mol}^{-1}$ over the true one, which is slightly bent.^[12] Moreover, for the sake of reducing the number of VB structures, both π systems were described as delocalized MOs, unlike the σ orbitals which remained localized AOs. It can be seen in Scheme 3 that the calculated weights of all four VB structures are significant and of the same order of magnitude, as was found for XeF_2 in previous work.^[16] To validate this picture, we also calculated the dissociation energy of SF_2^* to $SF^* + F$, using a wavefunction made of structures 9–12, each complemented with additional

minor structures describing the fluctuation of π electrons (see details in the Supporting Information). The BOVB calculation yields a dissociation energy of $96.5 \text{ kcal mol}^{-1}$, in very good agreement with the CCSD(T) value of $100.5 \text{ kcal mol}^{-1}$ (Table 2), thus fully validating the bonding picture displayed in Scheme 3 and the CRP model for SF_2^* .

Table 2. Dissociation energies as calculated in VTZ basis set. Energies in kcal mol^{-1} relative to the separate fragments.		
	BOVB	CCSD(T)
$SF^* \rightarrow S + F$	26.3 ^[a]	31.0 ^[a]
$SF_2^* \rightarrow SF^* + F$	96.5 ^[b]	100.5 ^[b]
$SF_4 \rightarrow SF_2 + 2F$	136.9 ^[b]	141.6 ^[b]

[a] Spin-unrestricted calculations. [b] Spin-restricted open shell for the dissociation products.

The hypervalent SF_4 molecule

The hypervalent SF_4 molecule is readily obtained by adding two F atoms to the vacant sites of SF_2^* , that is, to the two singly occupied π AOs of fluorine. The new SF bonds are perpendicular to the FSF axis and nearly perpendicular to each other, giving the molecule a butterfly shape, as shown in Figure 1. As these two equatorial SF bonds are classical two-electron bonds, they are shorter than the axial ones, which are hypervalent.

The VB structures of SF_4 are analogous to structures 9–12 of SF_2^* in Scheme 3, and are derived from the latter by replacing the singly occupied π AOs of sulfur with SF bonds. The calculated weights are displayed in Table 3, and can be seen to be rather similar to those of SF_2^* and XeF_2 , with significant contributions of all four VB structures, in the range 0.17–0.31.

As was done for SF_2^* , the validity of this four-structure picture for SF_4 can be checked by calculating its dissociation energy into $SF_2 + 2F$, following Equation (5), in which the two axial F atoms are extracted. This reaction leads to SF_2 in its 1A_1 ground state (bent geometry, see Supporting Information).

The BOVB-calculated value, $136.9 \text{ kcal mol}^{-1}$, is in very good agreement with the CCSD(T)-calculated value in the same basis

Figure 1. Geometries of a) SF_2^* (3B_1), b) SF_4 , c) PF_5 , and d) ClF_3 , along with selected bond lengths (in Å). Linear F–A–F are made perfectly linear.

Table 3. Weights of structures 9–12 for the series of isoelectronic molecules FAF (A = S, PF_3 , SF_2 , ClF_3 , Xe) in the framework of the Coulson–Rundle–Pimentel (3c–4e) model.					
	A = S SF_2^*	A = PF_3 PF_5	A = SF_2 SF_4	A = ClF_3 ClF_3	A = Xe XeF_2 ^[a]
$F^- \cdot A^+ \cdot F^-$ (9)	0.242	0.254	0.275	0.280	0.279
$F^- A^+ \cdot \cdot F$ (10)	0.242	0.254	0.275	0.280	0.279
$F^- A^{2+} F^-$ (11)	0.204	0.207	0.226	0.168	0.252
$F^+ A F$ (12)	0.312	0.285	0.224	0.272	0.190

[a] From Ref. [16].

set, 141.6 kcal mol⁻¹, once again confirming the correctness of the four-structure CRP picture for SF₄.

Now that the pertinence of the CRP (3c–4e) model has been established for hypervalent SF₂^{*} and SF₄, the next question is whether or not this model is assisted by charge-shift bonding (i.e., by very large resonance energies) as was found for iso-electronic XeF₂.^[16] Table 4 shows that this is indeed the case, as the resonance energies associated with the mixture of the degenerate covalent structures **9** and **10** are as large as 118.6 and 134.4 kcal mol⁻¹, respectively, for SF₂^{*} and SF₄. Further mixing with the remaining structures **11** and **12** still reinforces the total resonance energy by about half of these quantities. These resonance energies are of the same order of magnitude, and even larger, than those found in XeF₂.

Table 4. Resonance energies arising from the mixing of structures 9–12 in the framework of the Coulson–Rundle–Pimentel (3c–4e) model.					
	SF ₂ [*]	PF ₃	SF ₄	ClF ₃	XeF ₂ ^[a]
<i>E</i> (9)– <i>E</i> (10)	118.6	100.4	134.4	110.3	82.9
<i>E</i> (9–10)– <i>E</i> (9–12)	64.9	43.5	66.9	63.9	70.1
[a] From Ref. [16].					

The hypervalent PF₅ and ClF₃ molecules

The generality of the model can be checked further by completing the series of isoelectronic hypervalent species in the second row of the periodic table. Thus, the bent central fragment ¹A₁ SF₂ in SF₄ can be replaced by planar PF₃ or by ClF. This leads to PF₅ with a trigonal bipyramidal geometry in the first case, and by T-shaped ClF₃ in the second (see Figure 1). It can be seen in Table 3 that the weights of structures **9–12** for PF₅ and ClF₃ are in the same range as those of SF₂^{*}, SF₄, and XeF₂. Moreover, the resonance energies arising from the mixing of **9** and **10**, or from the mixing of these two structures with the remaining ones, are very large in all cases (see Table 4) and of the same order of magnitude, confirming that the same unique model is valid for the whole series of electron-rich hypervalent molecules. In summary, this model is Coulson's VB version of the Rundle–Pimentel 3c–4e model [Eq. (1)], but assisted by charge-shift bonding, as revealed by the exceptionally large resonance energies. This latter model accounts for the amazingly large bonding energies of linear F–A–F linkages in AF_{*n*} species (A=P–Xe, *n*=5–2), which also involve classical polar-covalent equatorial AF bonds. This conclusion is supported by the direct interpretation of VB wavefunctions, the quality of which is guaranteed by their successful calculation of dissociation energies, which match the results of CCSD(T) calculations in the same basis sets. Now, it is certainly of interest to determine how the recently proposed “recoupled-pair bonding” (RPB) mechanism fits in the above model.

Is the recoupled-pair bonding theory consistent with the charge-shift-assisted Coulson–Rundle–Pimentel model?

Woon and Dunning have defined RPB as follows, in the case of SF₂^{*}: “A recoupled pair bond is formed when an electron in

a singly occupied ligand orbital recouples the pair in a formally doubly occupied lone pair of a central atom, forming a central atom–ligand bond orbital”.^[15] Actually, the very same situation is met when the singly occupied AO of a Ne⁺ cation recouples one of the lone pairs of neutral Ne, forming a well-documented 3e σ bond,^[22] denoted [Ne:·Ne]⁺, like many other rare gas or isoelectronic fragments. Therefore, the RPB mechanism in SF₂^{*} could be considered as a 3e bond from the GVB point of view. In that sense, there is no contradiction between the RPB model for SF₂^{*} and our description of this excited state of SF in terms of a 3e σ bond, except that we would add a strong bonding participation of the π systems, which can be viewed either as forming two additional 3e bonds, or as contributing through some strong dynamic π back-donation. Note, however, that this π-bonding contribution is crucial for the stability of SF₂^{*}.

For a 3c–4e linkage, for example, FSF₂^{*}, the RPB model describes the bonding as a 2e bond between the incoming F radical and the singly occupied antibonding orbital of SF₂^{*}.^[12] The resulting structure is made of two polar 2e bonds, and is called a “recoupled pair bond dyad”.^[15] For this dyad to be formed, the axial 3p_z AO of sulfur is decoupled into right and left lobe orbitals, which each form an SF bond. It should be noted that these two lobe orbitals are considered as distinct despite their strong overlap of 0.85, and that the RPB dyad is not a classical VB structure. However, it is compatible with our model described above, at least with structures **9–11**, as in both cases the interaction of the central S atom with each F atom is described as partly covalent and partly ionic. Thus, in a way, one might consider the RPB dyad as a condensed structure summarizing structures **9–12** in a single structure, and so is also the 3c–4e model of Weinhold and Landis, which is based on NBO theory.^[23]

On the other hand, the charge-shift-assisted Coulson–Rundle–Pimentel model that we propose provides more detailed information and extra insight. It allows, in particular, the estimation of the weights of each VB structure expressed in the classical chemist's language, and the resonance energies caused by the mixing of these structures. It is also endowed with a pleasing predictive power, as shown in the next section.

Why are some 3c–4e systems stable whereas others are not?

As stated above, the stability of a 3c–4e system in the CRP framework rests on the magnitude of the resonance energy arising from the mixing of the four VB structures of Equation (1), that is, **9–12** in Scheme 3. A first obvious feature that would favor large resonance energies would be the individual energy levels of these structures being not too different from each other. Coulson has already pointed out the importance of a low ionization potential for the central atom in such systems, for example, XeF₂, and of the electronegativity of the ligands so as to favor the electron transfer from A to X in structures **9** and **10**.^[18c] As a complement to Coulson's statement, our study emphasizes the contribution of the structure involving a doubly ionized central atom, such as **11** in Scheme 3, and

the concomitant necessity for a low second ionization potential of the central atom.

For the illustration of these points, Table 5 reports the first and second ionization potentials (IPs) for the central atom of some selected neutral hypercoordinated species of type AF_n , together with their stabilities relative to breaking of the hypervalent bonds. It can be seen that although the first IP is an important parameter for the stability of AF_n , the second IP is at

Table 5. Ionization potentials of the central atom of some hypercoordinated species, and their dissociation energies to normal-valent species + 2F. All energies in eV.				
Central atom A	1st IP of A ^[a]	2nd IP of A ^[a]	ΔE of dissociation	Ref.
P	10.5	19.7	$PF_5 \rightarrow PF_3 + 2F \Delta E = 8.4$	13
S	10.4	23.3	$SF_4 \rightarrow SF_2 + 2F \Delta E = 6.5$	12
Cl	13.0	23.8	$ClF_3 \rightarrow ClF + 2F \Delta E = 2.8$	14
Xe	12.1	21.2	$XeF_2 \rightarrow Xe + 2F \Delta E = 2.8$	24
Kr	14.0	24.4	$KrF_2 \rightarrow Kr + 2F \Delta E = 1.0$	25
Ar	15.8	27.6	ArF_2 unstable	
N	14.5	29.6	NF_5 unstable	
O	13.6	35.1	OF_4 unstable	
F	17.4	35.0	F_4 unstable	
Ne	21.6	41.0	NeF_2 unstable	

[a] Experimental values from Ref. [26].

least as important, and indeed marks the limit between stable and unstable systems, and in particular the first-row systems (NF_5 , OF_4 , F_4 , NeF_2). The reason for the “first-row exception” is therefore quite clear within the present model.

Extending the reasoning to anions, one may consider an X_3^- cluster ($X = H, F, Cl, Br, I$, etc.) as a central X^- anion surrounded by two X radicals. Now, given that any X^- anion is supposed to have rather low first and second IPs, the stabilities of the trihalogen anions F_3^- , Cl_3^- , Br_3^- and I_3^- are readily explained by our model, but what about the instability of H_3^- ? Here, we must consider the second factor that favors large resonance energies in a multistructure electronic system: charge-shift bonding.^[21]

Any symmetrical hypercoordinated species, say $[A-B-A']$, can be considered as an intermediate or transition state in the exchange reaction $AB + A' \rightarrow A + BA'$, in which AB and BA' are normal-valent species. Generally, when AB is bound by a classical covalent bond, the so-called transition state resonance energy (TSRE) arising from mixing between the two VB structures $A-B/A'$ and $A/B-A'$ in $[A-B-A']$ is about one half of the AB bonding energy or less.^[19] However, much larger resonance energies can be found if AB is bonded by a charge-shift bond. For example, the TSRE is 41 kcal mol⁻¹ in H_3^- , which is less than half the bonding energy of H_2 , but it is 38.9 kcal mol⁻¹ in F_3^- , which is slightly larger than the bonding energy of F_2 (Ref. [27]). Thus, a large TSRE in the hypercoordinated complex originates from the charge-shift character of the bond in the normal-valent compound. Now it has long been shown that a necessary condition for charge-shift bonding to occur is that at least one of the atoms involved in the bond bears a lone pair(s).^[21] This condition is met for all the stable hypervalent

species in Table 5 and by trihalogen anions, but not for H_3^- . Thus, whereas F_2 , for example, is charge-shift bonded, H_2 is a classical covalent bond, and it follows that F_3^- is stable but H_3^- is not.

Conclusion

Some typical hypervalent species of the 3c–4e type, SF_4 , PF_5 , ClF_3 , and the 3B_1 excited state of SF_2 , have been studied by means of a modern VB method. The $^4\Sigma^-$ state of SF, which is the building block of SF_n molecules, is shown to display a triple 3e bond, or, expressed differently, by a strong 3e σ bond assisted by dynamic π back-donation in both π systems, the latter being essential for the stability of this species. The addition of one F radical to this excited diatomic species leads to the description of linear SF_2 in its 3B_1 state in terms of four VB structures, which are shown by the VB calculation to have rather similar weights, a result that also holds for SF_4 , PF_5 , and ClF_3 . The validity of this simple picture is ensured by the fact that the simple and compact VB wavefunction, from which the qualitative model is established, yields dissociation energies in very good agreement with state-of-the-art reference calculations in the same basis set. Furthermore, it is shown that considerable resonance energies arise from the mixing of four VB structures, which explains the amazingly large bonding energies of these hypervalent species, although they violate the octet rule. Thus, the general model for hypervalence in electron-rich systems appears to be the VB version of the Rundle–Pimentel model, coupled with the presence of charge-shift bonding. This latter feature implies the following conditions for hypervalence to occur: 1) low ionization potentials for the central atom, not only the first but also the second IP, and 2) ligands being prone to charge-shift bonding in normal-valent species (i.e., being electronegative and bearing lone pairs). The lack of any of these features explains the many exceptions to the traditional MO-based Rundle–Pimentel model, such as the instability of first-row 3c–4e systems, as well as that of ArF_2 , H_3^- , and so on.

Upon extrapolation, it is easily deduced that the same model applies to SF_6 , made up of three F–S–F linear linkages, although performing actual VB calculations would lead to overly large wavefunctions in this case ($4 \times 4 \times 4 = 64$ structures). The model is also readily extrapolated to heavier central atoms below P–Cl and below Xe in the periodic table, and to chlorine ligands or other electronegative/lone-pair-bearing fragments rather than fluorine. Thus, replacing SF_2 in SF_4 by isoelectronic groups such as Kr, Rn, one obtains KrF_2 , RnF_2 , whereas with the PCl_3 fragment and Cl ligands one obtains PCl_5 , and so on; all these species and many others in which the abovementioned conditions for hypervalence are fulfilled are known hypervalent species, for which we predict that charge-shift bonding is important.

Methods Section

A many-electron system wavefunction in VB theory is expressed as a linear combination of Heitler–London–Slater–Pauling (HLSP) func-

tions, Ψ_K , as in Equation (6), in which Φ_K corresponds to “classical” VB structures and C_K are structural coefficients.

$$\Psi_K = \sum_K C_K \Phi_K \quad (6)$$

$$W_K = C_K^2 + \sum_{L \neq K} C_K C_L \langle \Phi_K | \Phi_L \rangle \quad (7)$$

The weights of the VB structures are defined by the Coulson–Chirgwin formula^[30] [Eq. (7)], which is the equivalent of a Mulliken population analysis in VB theory, in which $\langle \Phi_K | \Phi_L \rangle$ is the overlap integral of two VB structures.

An important feature of our VB calculations is that all the active orbitals, here the ones that are involved in the axial F–A bonds (A = P, S, Cl), are strictly localized on a single atom, as in the classical VB method, so as to ensure a clear correspondence between the mathematical expressions of the VB structures and their physical meaning, ionic or covalent.

There are several computational approaches for VB theory at the ab initio level.^[19] In the VB self-consistent-field (VBSCF) procedure,^[20] both the VB orbitals and structural coefficients are optimized simultaneously to minimize the total energy. The BOVB^[18] method improves the accuracy of VBSCF without increasing the number of VB structures Φ_K . This is done by allowing each VB structure to have its own specific set of orbitals during the optimization process such that they can differ from one VB structure to another. In this manner, the orbitals can fluctuate in size and shape so as to fit the instantaneous charges of the atoms on which they are located. The BOVB method has several levels of sophistication. In this work, we chose the most accurate level, the so-called “SD-BOVB” level (see details in Supporting Information). Many previous calculations have assessed the reliability of this BOVB level to provide bonding energies on a par with state-of-the-art computational methods and with experimental data.^[18,19] The BOVB calculations were carried out with the Xiamen Valence Bond (XMVB) program.^[28]

In addition to standard 6-31G* and cc-pvTZ basis sets for SF*, a triple-zeta basis set with core pseudopotentials,^[29] referred to as VTZ, was used for all compounds. More details on the BOVB methods, VB calculations, and on the geometries used are provided in the Supporting Information.

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Keywords: ab initio calculations • charge-shift bonding • hypervalent compounds • Rundle–Pimentel • valence bond theory

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